

## **STEADY STATE REDOX POTENTIAL OF IODINE/IODIDE SYSTEM FOR DETERMINATION OF ARSENIC IN SYNTHETICALLY POLLUTED WATER**

**D. B. PATIL\*, S.B. REWATKAR\* AND G. J. THAKUR \*\***

\*Department of Chemistry, Institute of Science, Nagpur 440 001, India

\*\*Department of Chemistry, Mohta Science College, Nagpur, India

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### **ABSTRACT**

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**An electrochemical method was devised to measure very low concentration of arsenic in synthetically polluted water. Steady state redox potential of iodine/iodide system was utilized to measure low concentration of arsenic. The method is highly precise, accurate and reproducible. It can measure concentration of arsenic in the range of 0.03 mg to 0.11 mg.**

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### **INTRODUCTION**

Arsenic is known to be noxious to human beings and animal. The toxicity of arsenic depends on its oxidation state and arsenic (III) is reported to be more toxic than other oxidation states'. The maximum allowed concentration of arsenic in drinking water<sup>2</sup> is 0.05 mg/L. Various methods are available for its determination (Cullen and Reimer, 1989; Bermejo-Barrera *et al.* 1998).

In present work we have described steady state redox potential of iodine/iodide system as a tool to measure very low concentration of arsenic in synthetically polluted water. In this system the reaction has been studied under conditions of production of iodine at controlled rate and its simultaneous consumption by arsenic (III), such that a steady state is attained. The iodine is generated by the well known second order (Jalezynski *et al.* 1925; Burgess and Lathem, 1969) reaction of persulphate and iodide. This is a slow reaction and from the measurement of its rate constant, the rate of production of iodine under the conditions of known concentrations of the reactants can be accurately determined. On the other hand, the reaction between tri-iodide ion and

arsenic (III) is very fast and therefore in presence of very low concentration of arsenic (III) a steady state is attained soon; in which the rate of production of iodine equals its rate of consumption.

The effective concentration of iodine at steady state can be estimated by measurement of the redox potential of iodine /iodide system, then from knowledge of rate of production of iodine and rate constant, it is possible to evaluate very low concentration of arsenic (III).

## MATERIALS AND METHODS

### Measurement of the rate of production of iodine

The reaction between iodide and persulphate is studied by conventional method. Stock solutions of 0.040 M potassium iodide and 0.020 M potassium persulphate are prepared in phosphate buffer of PH 6.0 and the ionic strength is kept at 0.15 M by adding requisite amount of sodium chloride. The solutions are kept in a thermostat at 25.0 °C, 100 mL of each solution are mixed and a stop-watch is started simultaneously. 10mL of the reaction mixture are pipetted out at various intervals of time and transferred to 100 ml of ice-cold water to arrest the reaction. The liberated iodine is immediately titrated against 0.005 M sodium thiosulphate using starch as an indicator.

The rate constant for the reaction was determined from the plot of  $1/(a-x)$  Versus time (Fig.1; Table. 1) and hence

$$\text{Rate of production of iodine} = k [S_2O_8^{2-}] [I^-]$$

### Measurement of redox potential of iodine / iodide system under steady state

A stock solution of potassium iodide (0.040 M) and another of potassium persulphate (0.020 M) containing  $1.50 \times 10^{-3}$  M arsenic (III) are prepared in PH 6.0 and ionic strength 0.15 M. 20 mL each of the solution is maintained at 25.0 °C and mixed thoroughly and simultaneously a stop-watch is stalled. After 30 Second a large platinum foil electrode and saturated calomel electrode are introduced into the solution. The emf is thereafter measured at intervals of 30 second with digital potentiometer.

The emf values were plotted versus concentration of arsenic (III) present at that instant. This gave linear curve and its extrapolation to zero time results in the redox potential E, due to effective concentration of iodine at that instant. Such extrapolation to zero time has the advantage that at that instant, the rate of production of iodine and the concentration of arsenic (III) are known most accurately. Such redox potentials of iodine / iodide system were determined for various concentrations of arsenic (III) ranging from  $2.0 \times 10^{-4}$  M to  $16.0 \times 10^{-4}$  M (Fig. 2, Table.2) and redox potentials were plotted versus arsenic (III) concentrations. It is a calibration curve for the determination of arsenic (III) in synthetically polluted water.

### Synthetically polluted water

Synthetically polluted water was prepared by dissolving required amount of arsenic (III) in one litre of distilled water. Concentration of this stock solution

was  $16 \times 10^{-4}$  M. From this stock solution, solutions, of various concentrations of arsenic (III) ranging from  $3.00 \times 10^{-4}$  M to  $13.0 \times 10^{-4}$  M were prepared. The redox potentials of iodine/iodide system with arsenic (III) solutions were measured and from calibration curve the concentrations of arsenic (III) were determined (Table 3).

## RESULT AND DISCUSSION

The rate constant for the reaction between the sodium thiosulphate and iodine was determined by conventional method, of titration. The results are presented in Table. 1. From the slope of the curve of

$$\frac{1}{(a-x)}$$

versus time (Fig. 1) the rate constant for this well known second order reaction was determined. The rate constant ( $k_2$ ) =  $\frac{1}{2} \times \text{slope} = 3.67 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ . With the help of this rate constant, it is possible to evaluate the rate of production of iodine at zero time ( $r_1$ )

$$\begin{aligned} \text{Rate of Production of iodine, } (r_1) &= k, [S_2O_8^{2-}] [I^-] \\ &= 3.61 \times 10^{-3} \times 0.02 \times 0.01 \\ &= 7.33 \times 10^{-7} \text{ M s}^{-1} \end{aligned}$$

The redox potential E, of iodine/iodide system measured at zero time for various concentration of arsenic (III) are presented in Table.2. Such determina-

**Table 1**  
Measurement of the rate of production of iodine

Initial concentration of persulphate	:	1.0x 10 <sup>-2</sup> M		
Initial concentration of iodine	:	2.0 x 10 <sup>-2</sup> M		
Ionic strength ( $\mu$ )	:	0.15 M		
Temperature	:	25.0°C		
pH	:	6.00		
Time t/s	Amount of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> required/mL	Concentration of Iodine x/10 <sup>-3</sup> M	(a - x)/10 <sup>-3</sup> M	$\frac{1}{(a-x)}$ /M <sup>-1</sup>
600	1.75	0.438	9.56	104.6
1200	3.30	0.825	9.13	108.9
1800	4.65	1.16	8.84	113.1
2400	6.00	1.50	8.50	117.6
3000	7.20	1.80	8.20	122.0
3600	8.35	2.09	7.91	126.4
4200	9.40	2.35	7.65	130.8
4800	10.4	2.60	7.40	135.2

The rate constant, ( $k_2$ ) =  $\frac{1}{2} \times \text{slop of } \frac{1}{(a-x)}$  versus time

$$= \frac{1}{2} \times 7.33 \times 10^{-3} \text{ s}^{-1} = 3.67 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$$

The rate of production of iodine at zero time, ( $r_1$ )

$$= 3.67 \times 10^{-3} \times 0.02 \times 0.01 = 7.33 \times 10^{-7} \text{ Ms}^{-1}$$

**Table 2**

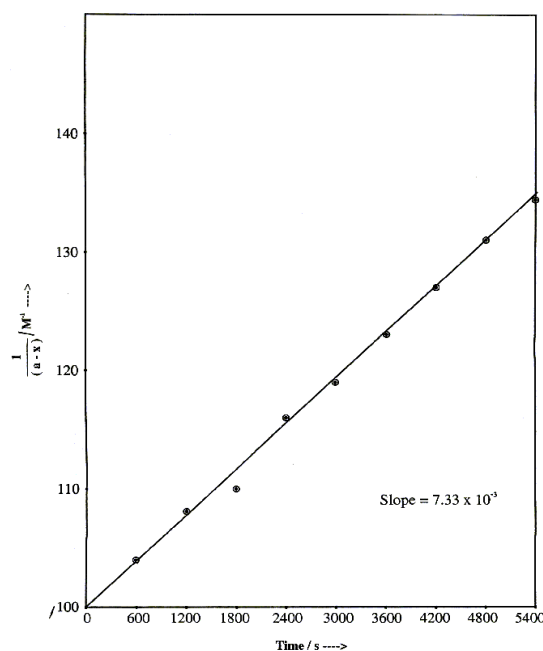
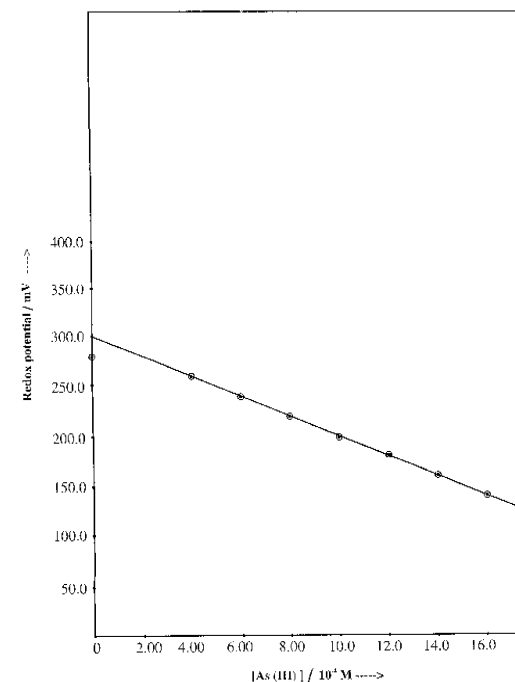
Redox potential of iodine / iodide system at zero time for various concentration of arsenic (III)

Arsenic (III) / $10^{-4}$ M	Redox potential of iodine/iodide system E / mV
2.00	280
4.00	270
8.00	220
12.0	180
16.0	145

**Table 3**

Amount of arsenic in synthetically polluted water

Concentration of Synthetically polluted water / $10^{-4}$ M	Redox potential of iodine /iodide system E./mV	Amount of arsenic in synthetically polluted water /mg
3.00	268.8	0.03
5.00	250.0	0.05
7.00	231.3	0.07
9.00	212.5	0.09
11.0	187.5	0.11

**Fig. 1** Rate of production of iodine at zero time**Fig. 2** Redox potentials of iodine /iodide system at zero time

tions at zero time has the advantage that at that instant the rate of production of iodine and the concentration of arsenic (III) are known most accurately. If one plots these redox potentials versus concentration of arsenic (III), it can work as a calibration curve for determinations of arsenic (III) for unknown samples. The redox potentials of various concentration of arsenic in synthetically polluted water, ranging from  $3.00 \times 10^{-4}$  M to  $11.0 \times 10^{-4}$  M were found to be 268.8 mV to 187.5 mV. The corresponding amount of arsenic was ranging from 0.03 mg to 0.11 mg.

## CONCLUSION

The work provides very precise method to determine very low concentration of arsenic in polluted water. It gives important method to environmentalists to measure arsenic in drinking water.

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